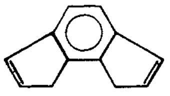
of polyfused cyclopentanoid systems we have examined the preparative value of path b in Scheme I and now wish to report our preliminary findings which detail a convenient one-step synthesis of 1 in 8–12% yield from commercially available starting materials.

Generation of tetraene 2 by path b would appear to require a reaction between 7-norbornadienyl cation and cyclopentadienyl anion; however, for convenience we favored the in situ formation of these reactive partners from appropriately stabilized precursors in a moderately polar aprotic solvent. Thallium cyclopentadienide (TlCp) was chosen as the cyclopentadienyl anion precursor on the basis of thermal stability and possible catalytic role of the metal ion on ionization of a suitable 7-norbornadienyl substrate, e.g., 7-norbornadienyl chloride (**6**-Cl). Accordingly, solutions of **6**-Cl in dry diglyme containing 10–80% molar excess of suspended TlCp were heated at 150 °C for 3–4 h under nitrogen and the reaction products separated from the thallium salts. Chromatography of the crude reaction product on silica gel with pentane afforded an initial fraction containing only diene **1** and dicyclopentadiene, a side product from decomposition of TlCp. Preparative GLC separation afforded pure **1**: ^{1}H NMR ($CDCl_3$) δ 5.79 (t, 4 H, J = 2.0 Hz), 2.85 (q, 4 H, J = 2 Hz), 2.43 (m, 2 H), and 1.80 (t, 2 H, J = 2.2 Hz); ^{13}C NMR ($CDCl_3$) 49.08, 60.58, 61.64, and 132.51 ppm from TMS; mass spectrum (70 eV) m/e (rel intensity) 156 (16.4), 155 (28.6), 154 (4.8), 152 (16.7), 141 (22.2), 128 (20.6), 115 (29.7), 91 (100), and 78 (21.5). The mass spectrum of **1** was unusual in that it indicated successive loss of one, two, and four hydrogen atoms from the parent ion to form a $C_{12}H_8$ ion (accurate mass) which most reasonably has the acenaphthylene structure.

The later pentane fractions from the original silica gel chromatography contained a third material along with minor contaminants which were removed by preparative GLC separation. Analysis of the separated material on a capillary column revealed at least two incompletely separated components in ~1:1 ratio. The proton spectrum ($CDCl_3$) showed an aromatic two proton singlet at δ 7.16, a set of complex, but sharply defined, two-proton olefinic multiplets at 6.7–7.0 and 6.2–6.6, and a pair of allylic triplets (J = 1.7 Hz) at 3.35 and 3.24 integrating for a total of four protons. This spectrum compares favorably with the published[5] spectrum for a mixture of dihydro-*as*-indacenes **7** and **8** (and possibly **9**). The mass spectrum [70 eV, m/e (rel intensity) 154 (82.5), 153 (100), 152 (45.4), 77 (10.8), 76.5 (8.4), and 76 (31.6)] is entirely consistent with this assignment.



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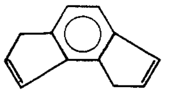

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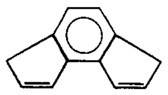

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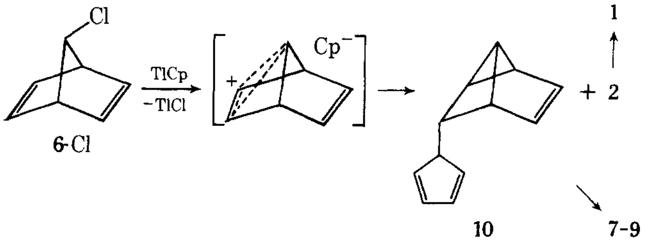
Altogether some six–eight reactions were carried out in diglyme (150 °C) according to the described procedure and employing 0.5 g, 1.0 g, or 2.0 g of **6**-Cl. Despite variations in the workup procedure the yield of diene **1** after silica gel chromatography consistently averaged ~100 mg/g of **6**-Cl (NMR or GLC analysis).[6] Thus the preparation of **1** on the gram scale by this method is entirely feasible. Furthermore, if analytical grade **1** is not required, material of at least 90–95% purity can be obtained by careful chromatography on silica gel with pentane, **1** eluting just prior to dicyclopentadiene.

Although the yield of diene **1** was consistent in the above reactions the total number of hydrocarbon products and the yield of the dihydro-*as*-indacenes appeared to vary with the age and quality of the TlCp reagent. With aged and slightly discolored samples of TlCp the ratio (NMR) of **1** to **7**, **8**, or **9** in the crude hydrocarbon product was 3–4:1. In experiments using freshly obtained TlCp[7] the yield of **7–9** was considerably reduced and a new hydrocarbon component, tentatively identified as a tetrahydro-*as*-indacene isomer, was detected by GLC and NMR.

The formation of diene **1**, together with the dihydro-*as*-indacenes **7–9**, may be satisfactorily rationalized by invoking initial generation of an intimate 7-norbornadienyl cation–cyclopentadienyl anion ion pair which suffers immediate and stereospecific ion collapse at either the C-7 or C-2 positions of the cation skeleton to afford **2** and the tricyclic hydrocarbon **10**. The latter hydrocarbon should undergo a cascading series of sigmatropic rearrangements to eventually afford an isomeric mixture of tetrahydro-*as*-indacenes which may be expected to at least partially dehydrogenate under the reaction conditions to give **7–9**.



Further exploration of this facile route into a complex series of C_{12} hydrocarbons is planned with particular emphasis on the reaction of preformed 7-norbornadienyl cations with cyclopentadienyl metal derivatives.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

References and Notes

(1) Abstracted in part from the Ph.D. Dissertation of J. F. Timberlake, University of Florida, Aug 1976.

(2) L. A. Paquette and M. J. Wyvratt, *J. Am. Chem. Soc.*, **96**, 4671 (1974).

(3) D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropulos, and E. Hedaya, *J. Am. Chem. Soc.*, **96**, 4673 (1974).

(4) Calculated from the yield data quoted in ref 2.

(5) T. J. Katz, V. Balogh, and J. Schulman, *J. Am. Chem. Soc.*, **90**, 734 (1968).

(6) The reaction may also be conducted at lower temperatures (e.g., refluxing glyme); however, extended reaction times are required (2–3 days) with no significant improvement in yields.

(7) Commercial grade TlCp was employed as received from Aldrich Chemical Co.

Merle A. Battiste,* John F. Timberlake
Department of Chemistry, University of Florida
Gainesville, Florida 32611

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Novel Substitution Reactions of 4-Chloro-4*H*-pyrazole Derivatives[1]

Summary: 4-Chloro-4*H*-pyrazoles and their mono and di-*N*-oxides have been prepared by treatment of the parent pyrazole with *tert*-butyl hypochlorite or chlorine. Treatment of these chlorides with methanolic base yields 4-methoxymethyl- or 3-methoxymethylpyrazoles, depending upon the structure of the starting materials.

Sir: Recently the synthesis of a 4-chloro-4*H*-pyrazole 1-oxide was reported.[2] We now have prepared the corresponding 4*H*-pyrazole and 4*H*-pyrazole 1,2-dioxide as well as some homologues and have observed some interesting substitution reactions of these compounds.

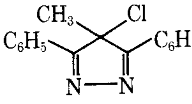
The series, 3,5-diphenyl-4-methyl-4-chloropyrazole (**1**)[3] and the corresponding 1-oxide (**2**) and 1,2-dioxide (**3**), has been

Table I. Elemental Analyses[a]

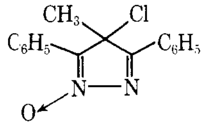
	Calcd, %				Found, %			
Compd	C	H	N	Cl	C	H	N	Cl
1	71.51	4.88	10.42	13.19	71.38	4.91	10.60	13.11
2	67.49	4.60	9.84		67.52	4.72	10.10	
3	63.90	4.36	9.31	11.79	65.70	4.47	9.36	11.98
4	77.25	6.10	10.60		77.25	6.22	10.68	
5	72.84	5.75	9.99		72.73	5.94	9.97	
6	68.91	5.44	9.45		68.62	5.38	9.60	
8	64.87	4.80	8.90	11.26	64.66	4.86	8.89	11.54
9	63.90	4.36	9.31	11.79	63.70	4.47	9.36	11.98

[a] Compounds **10** and **11** were analyzed by mass spectrometer peak matching because only small amounts were available. Calcd for $C_{18}H_{18}N_2O_3$ (**10**): 310.1318. Found: 310.1283. Calcd for $C_{17}H_{10}N_2O_3$ (**11**): 296.1162. Found: 296.1122.

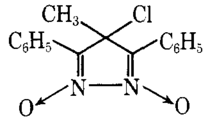
obtained by the action of *tert*-butyl hypochlorite or gaseous chlorine on the parent heterocycle.[4] All react with methanolic sodium hydroxide[5] to produce the corresponding 4-methoxymethylpyrazole derivatives, **4**, **5**, and **6**,[6] in yields of 80–95%. These transformations are accompanied by the disappearance of the CCH_3 (δ 2.00–2.18) groups from the NMR spectra, the appearance of OCH_3 (3.42) groups, and the appearance of the low field NH and OH resonances (13.1).



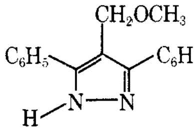
1, mp 115–117 °C



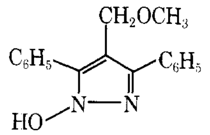
2, mp 109–111 °C



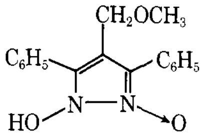
3, mp 140–142 °C



4, mp 181–183 °C

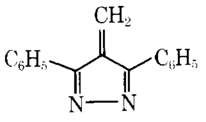


5, mp 157–158 °C



6, mp 183–184 °C

It seems likely that these reactions proceed by an elimination–addition mechanism with the diazafulvene **7** (and its *N*-oxide derivatives) as an intermediate. Burgess and Sanchez have reported the synthesis of the diphenylmethylene analogue of **7** and its reaction with methanol to yield the 4-methoxydiphenylmethylpyrazole.[7]



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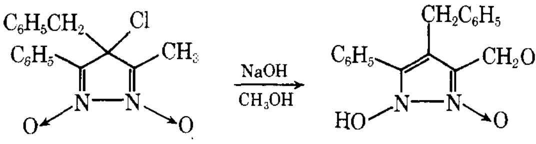
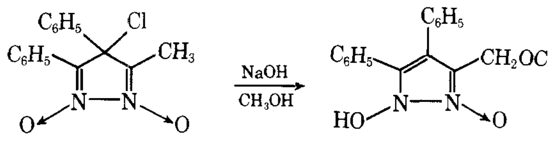
In a somewhat more unusual reaction, treatment of chlorides **8** and **9** in the same manner led to side-chain substitution in the 3-methyl group yielding compounds **10** and **11**. This result suggests that the enhanced acidity of these methyl groups leads to the formation of the 3-methylene derivative **12** in these cases.[8] The yields were much lower in these two examples and it is apparent that other destructive base-catalyzed reactions operate concurrently. Elemental analyses are given in Table I.



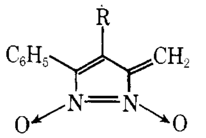
8, mp 126–127 °C

10



9, mp 127–128 °C

11



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References and Notes

(1) This research was supported in part by a grant from the National Cancer Institute, National Institutes of Health, Grant No. CA-10742.
(2) J. P. Freeman and E. Janiga, *J. Org. Chem.*, **39**, 2663 (1974).
(3) A series of unstable 4-bromo-4*H*-pyrazoles has been reported: P. Bouchet, J. Elguero, R. Jacquier, and F. Frissier, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **269**, 570 (1969).
(4) 1-Hydroxypyrazoles and 1-hydroxypyrazole 2-oxides have been reported: J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, **34**, 194 (1969).
(5) Compound **3** gave the corresponding ethyl ether when ethanolic NaOH was used.
(6) Treatment of 3,4,5-trimethylpyrazole with bromine in methanol produces 3-methoxy-3,4,5-trimethyl-3*H*-pyrazole: G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966).
(7) E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, **39**, 940 (1974).
(8) Steric factors also must be involved in the case of compound **8**, since its 4-methyl analogue undergoes the normal reaction leading to the 4-methoxymethyl derivative.

Jeremiah P. Freeman,* John F. Lorenc
Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

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The Reaction of Superoxide with Hydrazines, Hydrazones, and Related Compounds[1]

Summary. Potassium superoxide reacts with various hydrazo compounds and certain related substances in a variety of ways: monosubstituted arylhydrazines are readily oxidized in a reaction which appears to involve free aryl radicals; 1,2-diarylhydrazines are converted to the corresponding azo compound; certain 1,1-disubstituted hydrazines are oxidized to *N*-nitroso amines; and certain hydrazones are converted into the corresponding azine.

Sir: The autoxidation of hydrazines and certain related substances is a well-known but little understood reaction.[2] The redox nature of such processes suggests the possibility that superoxide may be involved.[3,4] In an effort to define the potential role of superoxide in these reactions we have examined